HE EFFECT OF DILUTION ON HE HYDROGEN POTENTIALS OF ETIC ACID AND "STANDARD ACETATE" SOLUTIONS

BY

G. S. WALPOLE, D.Sc., F.I.C.

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The Wellcome Physiological Research Laboratories
Brockwell Hall
Herne Hill
London, S.E.

CXXXIV.—*The Effect of Dilution on the Hydrogen Potentials of Acetic Acid and " Standard Acetate " Solutions.*

By George Stanley Walpole.

The measurements described in this paper form a continuation of the work already detailed in the preceding one. Several alterations were made in the technique and apparatus employed with a view to increase if possible the accuracy of the results.

The potentiometer used was made by Tinsley, and had two dials. The first read 0·1 volt for each coil, and the second, acting as a vernier on the Thomson-Varley slide principle, read 0·01 volt for each coil. A light travelling contact of platinum, actuated from outside the instrument by a silk cord, pressed evenly on two similarly placed wires. One of these was the slide wire of the potentiometer. The other was a similar wire, to which the electrometer was connected. All junction and thermo-electric effects were therefore neutralised. Three cm. of the slide wire corresponded with a millivolt in the potentiometer reading without the use of a multiplying shunt. The instrument was guaranteed correct to 1 in

100,000 at the reading 1 volt, and certainly contained no inaccuracy which could affect these measurements.

The perfect insulation of the instrument in addition to the precaution of isolating all parts of the apparatus on paraffin banished the "zero movement" of the electrometer so completely that even with the powerful optical arrangement employed it could not be detected. On one or two damp days, however, a movement of the meniscus could be observed on opening the key short-circuiting the electrometer, and the work was, for that reason, temporarily suspended.

The electrode vessel employed was entirely of silica, and was made specially for these determinations. It was of the conventional
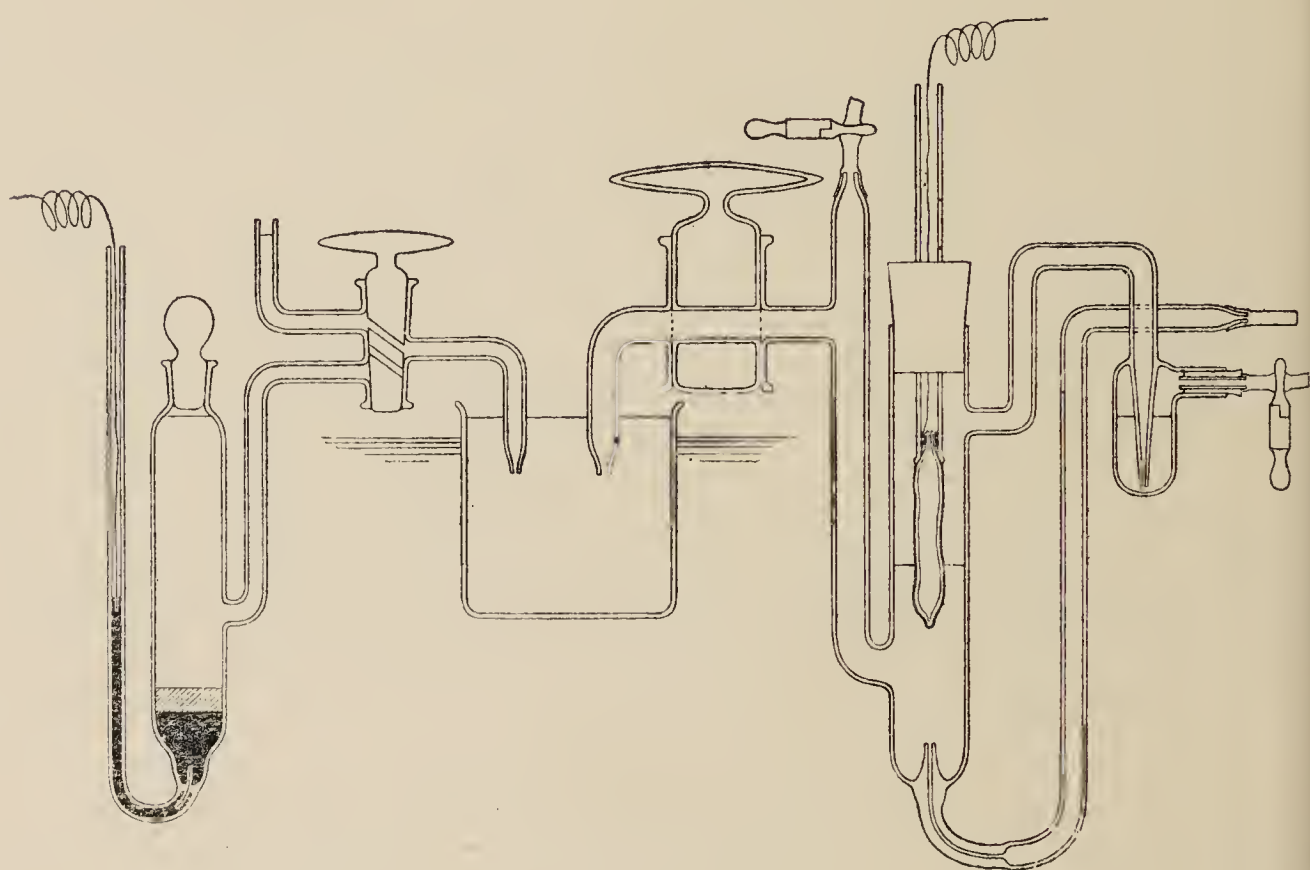
pattern, except that the side-tube connecting its contents with the saturated solution of potassium chloride was of wide bore (7·5 mm.) and carried a full-bore silica tap. This was essential in view of the low conductivity of some of the solutions to be examined. The electrodes themselves were made by blackening a film of platinum burnt on to the surface of the hardest Jena glass. In this way it was arranged that when once the solution was placed inside the electrode vessel it came into contact with nothing but platinum and silica.

In order to make an observation, the carefully prepared electrode, which had been standing in the experimental fluid, was transferred to the electrode vessel, which was filled to such an extent that the blackened platinum surface was completely covered. Hydrogen

was passed through the fluid for twenty-five minutes, and then so much of the fluid forced out through the side-tube that only one third of the electrode remained immersed. After another five minutes, during which hydrogen was passed slowly, the stream of gas was stopped and a reading taken. It was demanded of every electrode employed that it should then give at once a potential constant to 0.05 millivolt for at least half an hour, and that another electrode should give within less than 0.10 millivolt the same reading when they were tested in the same well-conducting fluid of known stability of reaction, for example, "standard acetate." Electrodes of the type used satisfying these conditions could be prepared with comparative ease.

The Silica Syndicate of London, who made the silica vessel, kindly prepared some silica electrodes with platinum burnt on the surface, but these were not so successful. Possibly this was because it was impossible to lead the platinum film through the silica as had been done with the glass electrodes. They were therefore forced to make contact between the inside and the outside of the electrode by means of a fine metallic wire leading through the silica, thus sacrificing what would appear to be the cause of the superiority of these electrodes, namely, the uniform thinness of the layer of metallic platinum on which the platinum black is deposited.

All hydrogen potential readings were corrected for barometric variation. If the barometer reading was x mm., then $(760 - x)\,0.017$ millivolt was added to the potentiometer reading obtained, due attention being paid to the algebraic sign. This correction during these experiments never exceeded 0.15 millivolt, and was usually much less.

The method of working was to determine all potentials against a special $0.10N$-calomel electrode G. In order to avoid any risk of variation in the potential of this electrode in use, the Wilsmore two-way tap device was employed, and the vessel clamped so firmly that the daily rinsing of the side-tube could be performed without mechanical shock or vibration. The copper wire leading into the mercury in the second side-tube was not disturbed at any time. The calomel and the $0.10N$-potassium chloride solution in the electrode vessel were prepared with the usual precautions. The side-tubes from both this electrode and the hydrogen electrode dipped into a vessel containing $4.10N$-potassium chloride. The water-bath containing this vessel and the calomel electrode was kept at $18° \pm 0.1°$ for several hours before any readings were taken and during the observations, so that the calomel electrode might be given every opportunity of giving an absolutely constant value. At first a saturated potassium chloride electrode (A) was used as a check on the

0·10N-potassium chloride electrode G. This was useful in that it gave an accurate check on the correctness of the temperature of the bath. A rise of 0·10° in the temperature of the two electrodes increases the difference of potential by 0·05 millivolt.

Throughout these measurements the $E.M.F.$ of the cell

(Pt) | H_2, "standard acetate solution" | saturated KCl | 0·10N-KCl, Hg_2Cl_2 | Hg

was repeatedly determined as a check on the "standard acetate," the hydrogen electrodes themselves, and the 0·10N-calomel electrode G. With hydrogen electrodes satisfying the conditions described, the value obtained was uniformly 0·6046±0·0001 volt, indicating that the calomel electrode G gave a constant potential, differing by perhaps 0·10 millivolt from the mean value given by the four control electrodes alluded to in the preceding paper.

One factor contributed largely to the accuracy of these measurements, namely, the hot, dry weather experienced. This made possible excellent insulation of the whole of the electrical apparatus. On the other hand, before measuring out definite volumes of solution it was necessary to cool the solutions used to 15°. The bath was kept at 18° by means of a rotary pump driven by a turbine. This drew water from the bottom of the bath, and after passing it in turn through a lead coil immersed in ice and water, a heating spiral, and a toluene gas regulator, returned it to the top again. The stream was sufficient in volume to ensure efficient stirring of the bath.

The N-acetic acid solutions were prepared as described in the preceding paper. Both the first and last samples from the N-acetic acid bottle were titrated against a carefully guarded N-hydrochloric acid solution by means of 0·20N-baryta with a discrepancy of only 1 in 1000 between the two results.

The N-sodium acetate solution was adjusted by the electrometric method previously described. The results of the experiments show that given pure sodium acetate and pure acetic acid, "standard acetate" solution may be readily produced with such accuracy that, in spite of its small diffusion potential and the consequent small time-change of that potential, no differences in composition of two samples can be detected by the most searching hydrogen potential measurements possible in the present state of our knowledge.

All solutions were made up with water of less than 5 gemmhos specific conductivity. For the great majority of these determinations the result would not have been affected if the highest grade "conductivity" water had been used instead.

The contact potential measurements were made by the method described in the preceding paper.

The Change of the Hydrogen Potential of Acetic Acid on Dilution.

In the table below the results of these measurements are given. The first column contains the volume of solution in litres containing 60·03 grams of acetic acid for each dilution examined.

TABLE I.

$v = 1/C_1$.	E.M.F.	d.	$(E.M.F. - d)_1$.		k_a.	
4	0·49005	0·0003	0·48975	0·00000	$21\cdot7.10^{-6}$	$0\cdot17.10^{-6}$
5	0·49300	0·0002	0·49280	−0·00007	$21\cdot2.10^{-6}$	$0\cdot17.10^{-6}$
10	0·50240	0·0002	0·50220	−0·00022	$20\cdot2.10^{-6}$	$0\cdot16.10^{-6}$
20	0·51115	0·0001	0·51105	+0·00018	$20\cdot0.10^{-6}$	$0\cdot16.10^{-6}$
25	0·51395	0·0001	0·51385	+0·00037	$20\cdot0.10^{-6}$	$0\cdot16.10^{-6}$
40	0·52040	0·0001	0·52030	+0·00019	$19\cdot2.10^{-6}$	$0\cdot15.10^{-6}$
50	0·52350	0·0001	0·52340	+0·00007	$18\cdot9.10^{-6}$	$0\cdot14.10^{-6}$
100	0·53282	0·0001	0·53273	0·00000	$18\cdot1.10^{-6}$	$0\cdot14.10^{-6}$
400	0·55105	0·0001	0·55095	+0·00028	$17\cdot8.10^{-6}$	$0\cdot14.10^{-6}$
500	0·55430	0·0001	0·55420	0·00000	$17\cdot2.10^{-6}$	$0\cdot13.10^{-6}$
1000			(0·56347)		$(17\cdot0.10^{-6})$	

The electromotive forces of the cells

$$\text{Pt} \mid \text{H}_2, \text{ acetic acid solution} \mid 4\cdot10N\text{-KCl} \mid 0\cdot10N\text{-KCl}, \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$$

are given in column 2. In column 3 are the diffusion potential differences (d) against $4\cdot10N$-potassium chloride solution. They were determined in the manner described, and although they are undoubtedly very small and their inaccuracy affects to no appreciable extent the conclusions which can be drawn from these observations, they resemble all other measurements of contact potential in that they cannot be accepted without a certain reservation. When the values of $(E.M.F. - d)_1$ were plotted against $\log v$ on squared paper it was seen that they approximated very closely to a straight line. This line could be represented by the formula:

$$\frac{\log v - 0\cdot60206}{(E.M.F. - d)_1 - 0\cdot48975} = 32\cdot53 \quad . \quad . \quad . \quad (1).$$

In column 5 are given the quantities which would have to be added to the observed E.M.F.'s to obtain figures for $(E.M.F. - d)_1$ satisfying equation (1). It is seen that with a maximum error of 0·37 millivolt in one direction and 0·30 millivolt in the other, $(E.M.F. - d)_1$ is a linear function of the logarithm of the dilution.

Directly from the equation representing the equilibrium between acetic acid and the ions obtained by its dissociation, that is,

$$\text{H}^{\cdot} + \text{Ac}' \rightleftharpoons \text{HAc},$$
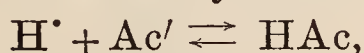
we may, since it is a weak electrolyte, write

$$[\text{H}^{\cdot}][\text{Ac}'] = k_a[\text{HAc}]$$

or

$$k_a = \frac{[\text{H}^{\cdot}]^2}{C - [\text{H}^{\cdot}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

where [H·] and [Ac′] are respectively the hydrogen- and acetic-ion concentrations, [HAc] is the concentration of undissociated acetic acid, and C equals the total concentration of acetic acid. The values of ⌈H·⌉ can be calculated from the hydrogen potentials $(E.M.F. - d)$, given in table I, $\epsilon_h = 0.3377$, and the constant 0.0577, by the application of the well-known energy equation quoted in the preceding paper. Since C is known, the values of k_a for different dilutions can be calculated. The results of calculations performed in this manner are given in column 6 of the same table.

It is seen at once that a minute alteration in the value of the $E.M.F.$ will correspond with a large change in the value of k_a, the dissociation constant of acetic acid. In order to facilitate the examination of these results the alteration in the value of k_a obtained by altering the $E.M.F.$ 0.10 millivolt is given in column 7. At this point it will be convenient to mention a discrepancy between these results and those of Loomis and Acree (*Amer. Chem. J.*, 1911, **46**, 585) with respect to the $E.M.F.$ of acetic acid. As the mean of several concordant results, 0.4930 may be taken as their value against the $0.10N$-calomel electrode for $0.25N$-acetic acid, the connecting fluid being $4.10N$-potassium chloride. This is 3 millivolts higher than the value found by the present author, and corresponds with a dissociation constant of 16.7×10^{-6} if the same values for d and ϵ_h are taken as those used previously by the author. The acetic acid from which the solutions were made was found free from formic acid, and it is suggested that possibly Loomis and Acree's sample contained traces of higher homologous acids, although in view of the care and high order of accuracy with which their measurements were made this attempt at explanation of the discrepancy is put forward with the greatest diffidence.

The Change of Hydrogen Potential of "Standard Acetate" on Dilution.

"Standard acetate" solution is a solution decinormal with respect to both acetic acid and sodium acetate. The results obtained, proceeding precisely as with acetic acid, are given in table II.

TABLE II.

$v = 1/C.$	E.M.F.	d.	(E.M.F. — d).	x.
5	60360	0.00015	60345	0.00000
10	60460	0.00015	60445	0.00001
25	60585	0.00010	60575	0.00037
50	60683	0.00005	60678	0.00049
62.5	60735	0.00000	60735	0.00028
100	60798	0.00000	60798	0.00044
200	60923	0.00000	60923	0.00033
500	61100	0.00000	61100	0.00008
1000	61222	0.00000	61222?	0.00000

In column 1 v represents, as before, the volume occupied by 1 gram-molecule of acetic acid; columns 2, 3, and 4 contain data derived in the same way as in the table for dilutions of acetic acid alone.

If the values of $(E.M.F. - d)$ are plotted against $\log v$, a straight line does not result, but a curve, the nature of which may be judged from the figures in column 5. These were calculated from the formula:

$$x = \frac{\log v - \log 5}{262 \cdot 1} + 0 \cdot 60345 - (E.M.F. - d) \quad . \quad . \quad . \quad (7)$$

and represent the $E.M.F.$'s in volts which must be added to the $E.M.F.$ observed, to obtain those values which would have been obtained if the function relating $(E.M.F. - d)$ and $\log v$ had been linear, and if the straight line passed through the observed points corresponding with $v = 5$ and $v = 1000$.

Determination of the Dissociation Constant of Acetic Acid at Different Concentrations, in Terms of the dissociation of Sodium Acetate at the same concentration, and independently of the E.M.F. of any Auxiliary Electrode.

From the $E.M.F.$ of a hypothetical cell made up of two hydrogen electrodes immersed, one in an acetic acid solution and the other in an acetic acid–sodium acetate mixture, it is simple to calculate the value of k_a in terms of α. This determination is independent of the $E.M.F.$ of any auxiliary half cell; the only assumptions are the Ostwald energy relationship involving the constants R, F, T, and the law of mass action as applying to acetic acid.

The values of $(E.M.F. - d)_1$ and $(E.M.F. - d)$ in tables I and II preceding provide data for the $E.M.F.$'s of a number of these hypothetical cells. Any acetic acid solution of hydrogen electrode potential $(E.M.F. - d)_1$ may be considered linked, without contact potential, to any acetic acid–acetate mixture of hydrogen electrode potential $(E.M.F. - d)$ in table II. The $E.M.F.$ of the cells so formed is $(E.M.F. - d) - (E.M.F. - d)_1$, and may be written E_2.

With reference to the data in table II we may write:

$$(E.M.F. - d) = 0 \cdot 3377 + 0 \cdot 0577 \log \frac{\alpha C}{k_a C} \quad . \quad . \quad . \quad (8)$$

for the solutions, being dilutions of "standard acetate," contain acetic acid and sodium acetate in equal concentrations. Similarly, in table I:

$$(E.M.F. - d)_1 = 0 \cdot 3377 + 0 \cdot 0577 \log \frac{1}{\sqrt{k_a C_1}} \quad . \quad . \quad (9).$$

Choosing the data from each table so that for each cell considered $C=C_1$,

$$(E.M.F. - d) - (E.M.F. - d)_1 = E_2 = 0.0577 \log \frac{aC}{\sqrt{k_a C}}$$

or

$$\log k_a = 2\left(\log aC - \tfrac{1}{2}\log C - \frac{E_2}{0.0577}\right) \quad . \quad . \quad . \quad (10).$$

Equations 8 and 9 above, however, are not as accurate as it is possible to make them, although if they are improved E_2 is no longer absolutely independent of the value of ϵ_h. The more accurate equations are (see preceding paper):

$$(E.M.F. - d) = 0.3377 + 0.0577 \log \frac{a'C + [H^{\cdot}]}{k_a(C - [H^{\cdot}])}$$

$$(E.M.F. - d)_1 = 0.3377 + 0.0577 \log \frac{1}{\sqrt{k_a(C - [H^{\cdot}]_1)}}$$

and in the special case where $C = C_1$,

$$E_2 = 0.0577 \log \left(\frac{\frac{\mu_{[Ac']}}{\mu_\alpha} C' + [H^{\cdot}]}{k_a(C - [H^{\cdot}])} \cdot \sqrt{k_a(C - [H^{\cdot}]_1)} \right) \quad . \quad (11).$$

Now $[H^{\cdot}]$ and $[H^{\cdot}]_1$ are comparatively small quantities, and, as they are placed in this equation, an error in their determination resulting from a possible incorrectness of ϵ_h will be without effect, so we may substitute the actual values of $[H^{\cdot}]$ and $[H^{\cdot}]_1$ calculated in the ordinary way into this equation, and still regard it as a determination of k_a in terms of a, at the same value of v, independent of the exactness of the value of ϵ_h.

The values of k_a obtained, using equation (11), Kohlrausch's conductivity data, as before, ($\mu_\alpha = 76.8$), and the data from tables I and II, are given below:

$v.$	$k_a.$	k_a (Jones).
5	$17.0.10^{-6}$	$17.3.10^{-6}$
10	$18.4.10^{-6}$	$18.2.10^{-6}$
25	$18.8.10^{-6}$	$18.5.10^{-6}$
50	$19.9.10^{-6}$	$18.4.10^{-6}$
100	$20.8.10^{-6}$	$18.3.10^{-6}$
500	$19.0.10^{-6}$	$18.0.10^{-6}$
1000	$18.4.10^{-6}$	$18.0.10^{-6}$

For comparison, the latest values for the dissociation constant of acetic acid by the conductivity method have been placed in the last column (Jones, *Reports Carnegie Institution*, No. 170).

Summary.

The relationship between the hydrogen potential of acetic acid and the logarithm of its dilution is strictly linear. Assuming that

the energy relationship holds, and that the law of mass action applies to acetic acid, and taking as data the constants at present accepted, the dissociation constant of acetic acid would appear to fall steadily with dilution.

Determinations of the dissociation constant of acetic acid in terms of the dissociation of sodium acetate have been made by hydrogen potential measurements, in which the accurate knowledge of the $E.M.F.$ of no subsiduary half electrode is involved. The figures taken for the dissociation of sodium acetate were calculated in the usual way from Kohlrausch's conductivity measurements. Assuming that they are correct, the values of the dissociation constant of acetic acid obtained in this way show a rise and a subsequent fall with dilution. The same rise and fall has been observed by Jones to a less marked extent in the values of k_a obtained by the conductivity method.

In exactly what direction the results obtained in this and the preceding paper can be applied to qualify the present generalisations with regard to the properties of electrolytes in solution is not at once evident. It would appear that the accuracy of the measurements is sufficiently high to make possible an attempt at the analysis of the discrepancies observed when the data for the dissociation of sodium acetate are more firmly established. Taking into account the magnification of the errors of observation in these calculations of k_a it is certain that the difficulties of providing sufficiently accurate data will disappear only when a higher order of accuracy is reached than is at present possible.

The hydrogen potential of "standard acetate" against the $0.10N$-calomel electrode has been redetermined. The result obtained is 0.6046 volt with saturated potassium chloride solution interposed between the two halves of the cell; corrected for contact potential it is 0.6045 volt.

I wish to express my obligations to Prof. S. P. L. Sörensen for his helpful suggestions.

Wellcome Physiological Research Laboratories,
            Herne Hill, London, S.E.